

IMPROVED DIFFERENTIATION OF SULFUR FORMS IN COALS BY
SELECTIVE DEGRADATION WITH PERCHLORIC ACID MIXTURES

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Keywords: sulfur forms in coal; coal analysis for sulfur;
perchloric acid dissolution of coal

INTRODUCTION

Recent work at the Ames Laboratory has resulted in proposing a promising new technique for determining sulfur forms in coal based upon the step-wise oxidation of coal with perchloric acid (1). Initial results on determination of sulfur forms by selective oxidation with perchloric acid have been very encouraging (2). Relatively sharp and reproducible delineations have been observed for sulfide, sulfate, pyritic, and organic sulfur in some cases. Other preliminary studies on model organosulfur compounds have shown it to be possible to differentiate between at least two groups of organic sulfur compounds by this technique (3). In more recent work, the reproducibility of these results has been confirmed, more detailed conditions for extracting selectively the various sulfur species have been specified, and more coal samples with higher organic sulfur content have been tested.

EXPERIMENTAL PROCEDURES

Based upon earlier observations of the behavior of coal, pyrite, and sulfate salts with boiling HClO_4 at various temperatures (1), a reaction scheme was developed for the direct determination of sulfur forms in coal which uses the variable oxidizing power of HClO_4 to dissolve selectively sulfur-containing components and convert them to sulfate for turbidimetric measurement. In the original procedure for the consecutive determination of sulfur forms in a single sample of coal (2), sulfate was extracted with a HClO_4 solution boiling at 120°C, pyrite with a HClO_4 solution boiling at 155°C, and organic sulfur with a solution of 9:1 HClO_4 - H_3PO_4 boiling at 205°C. In all 3 steps, sulfur-containing gases were trapped in 15% H_2O_2 , and sulfate was determined in the trap and in the aqueous filtrate. If any sulfide was present, it was captured and measured in the H_2O_2 -filled gas trap during the extraction of sulfate. For some coals, however, total sulfur recovered was slightly less than total sulfur in the coal (0.2-0.4% abs.). The low recovery could be due to: 1) incomplete absorption of sulfur-containing gases by the neutral H_2O_2 solution in the trap, 2) dissolution of some organosulfur compounds at 155°C without total conversion to sulfate, and 3) analytical factors, such as incomplete precipitation of BaSO_4 due to high acidity. For other coal samples, the discrepancy between pyritic and organic sulfur forms determined by the ASTM and the HClO_4 procedures was significant. Some of these possibilities have been tested experimentally in previous work (4-6).

RESULTS AND DISCUSSION

Determination of Sulfur Forms in Coal

Using the original procedure, the following results were obtained for sulfur forms in Illinois, Pittsburgh, and New Zealand coals (minus 60 mesh) and in another Illinois No. 6 coal (minus 200 mesh), as shown in Table 1. While for the minus 60-mesh coal samples the agreement between the HClO_4 and ASTM procedures for pyritic and organic sulfur forms is reasonable, it is quite divergent for the minus 200-mesh sample. Therefore, further tests were conducted to test the conditions for selective extraction of sulfur forms.

Table 1. Sulfur Form (in %) Determined by HClO_4 and ASTM Procedures

	Sulfate	Sulfide	Pyritic	Organic	Total
<u>Illinois No. 6 (-60 mesh)</u>					
HClO_4 (avg. of 4 detns.)	0.74	0.02	1.79	1.64	4.19
ASTM (1 detn.)	0.75	n.d.	1.69	1.77	4.21
<u>Pittsburgh No. 8 (-60 mesh)</u>					
HClO_4 (avg. of 2 detns.)	0.48	0.01	1.13	1.32	2.94
ASTM (1 detn.)	0.49	n.d.	1.18	1.47	3.14
<u>Charming Creek N.Z. (-60 mesh)</u>					
HClO_4 (1 detn.)	0.04	0.01	0.11	5.02	5.18
ASTM (1 detn.)	0.04	n.d.	0.02	5.38	5.44
<u>Illinois No. 6 (-200 mesh)</u>					
HClO_4 (avg. of 2 detns.)	0.24	0.04	3.27	1.38	4.93
ASTM (1 detn.)	0.20	n.d.	2.87	1.85	4.92

Dissolution of Sulfur from Coal as a Function of Temperature

The original procedure, based on extracting -60 mesh coal using the boiling point of the pure HClO_4 solution as the temperature guide, resulted in typical S-shaped dissolution curves, as shown previously (1) for an Illinois No. 6 coal sample containing 4.85% total sulfur (0.26% sulfate, 2.42% pyritic, and 2.17% organic sulfur). Although there was a lot of scatter for that -60 mesh coal, it was on the basis of such curves, as well as the behavior of pure pyrite and mineral sulfate, that the HClO_4 b.p. of 120, 155, and 203°C were selected for the extraction of sulfate, pyritic, and organic sulfur, respectively.

When the extraction procedure was repeated for another Illinois No. 6 coal, -200 mesh and containing 4.98% total sulfur (0.04% sulfate, 3.04% pyritic, and 1.90% organic sulfur), the much smoother curve depicted in Figure 1 was obtained. In this and all subsequent figures, the temperature of the reaction mixture (HClO_4 plus coal) is plotted. The curve shows a definite break at ~140-145°C, showing a clear delineation between pyritic and organic sulfur.

Analysis of Coal Residues After HClO_4 Extraction

In order to get additional information about the possible dissolution of organic sulfur and the oxidation of organic matter in the coal, the undissolved materials from HClO_4 extractions at several temperatures, as well as a sample of the raw coal, have been further analyzed for organically associated S, Cl, and O using our SEM-EDX procedure described earlier (7).

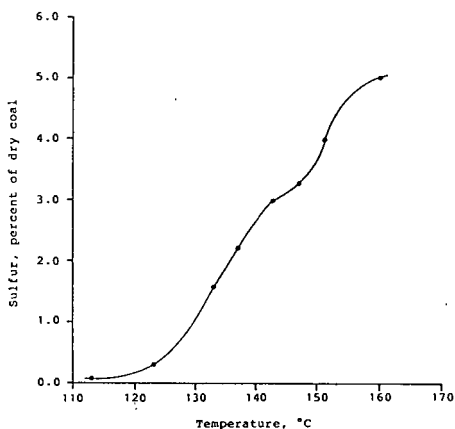


Figure 1. Total sulfur recovered (as percent of dry coal) as a function of reaction temperature for Illinois No. 6 coal (-200 mesh)

Because this technique measures organically bound elements on a dry, mineral matter-free (dmmf) basis, the results could not be directly compared to those obtained by the ASTM or HClO_4 procedures (the coal contained 28.8% ash). However, there were several interesting trends. First of all, it was evident that the organic sulfur content was fairly constant, within the experimental errors of this technique, until a temperature of about 147°C. At the same time, there was a significant increase in organic oxygen and chlorine as the temperature increased. This was not unexpected since the coal was being oxidized, and chlorination is known to occur during the perchloric acid degradation of organic compounds (3). When corrected for O and Cl content, the organic S content appeared to be fairly constant almost up to 151°C.

Dissolution of Iron During Extraction of Sulfur from Coal

The solutions from Illinois coal samples extracted for sulfur at different temperatures (Figure 1) were also analyzed for iron by atomic absorption spectrophotometry. The results are presented in Figure 2, and the amount of undissolved material is presented in Figure 3. It is evident that the amount of dissolved iron increases up to ~143°C and then becomes constant, indicating that all the pyrite has been dissolved before the coal matrix starts to be dissolved. Also, at 113°C, where only sulfate is extracted, pyrite is not dissolved.

Dissolution of Coal During Extraction of Sulfur

Figure 3 represents the weight loss for the same Illinois coal sample depicted in Figure 1. It is evident that the amount of undissolved material does not decrease until temperatures of ~143°C are reached, indicating that the organic matrix and the associated organic sulfur have not been leached out at a temperature at which pyrite has been dissolved. This is also corroborated by the color of the extracts, which are colorless or pale yellow until ~143°C

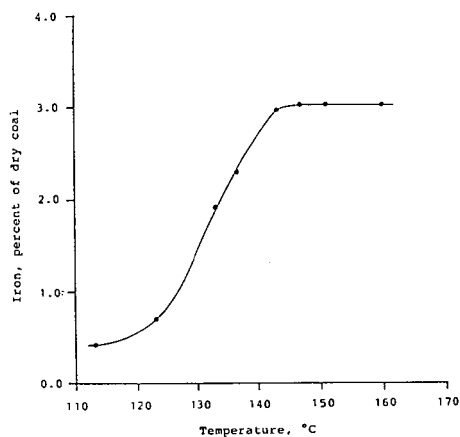


Figure 2. Dissolved iron (as percent of dry coal) as a function of reaction temperature for Illinois No. 6 coal (~200 mesh)

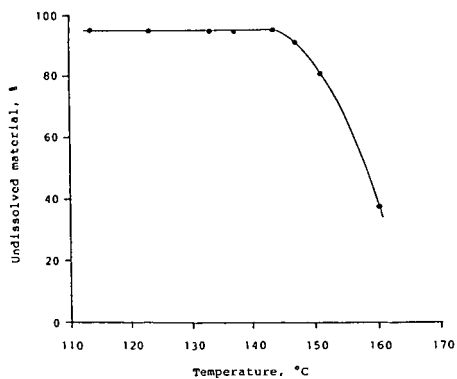


Figure 3. Undissolved material as a function of reaction temperature for Illinois No. 6 coal (~200 mesh)

and then become orange to deep-brown at higher temperatures at which coal begins to dissolve. Further details of these observations are described elsewhere (8).

New Procedure for Determination of Sulfur Forms

Based upon the results above, it was concluded that better delineation of sulfur forms could be obtained by employing lower temperatures for the dissolution steps, i.e., 110°C for sulfate and 143°C for pyrite sulfur. Applying this modified procedure to another sample of Illinois No. 6 coal gave the results presented in Table 2. It is evident that the agreement between these results and those from ASTM procedures is very good.

Table 2. Sulfur forms (percent of dry coal) in Illinois No. 6 (bottle 7) by HClO_4 procedure using new step-wise oxidation conditions.

S form	Mixture Temp. (°C)	% S (dry basis)				% S by ASTM (dry basis)
		Expt.1	Expt.2 ^a	Expt.3 ^a	Average	
Sulfate	110	0.07	0.07	0.07	0.07	0.04
Pyritic	143	2.99	2.91	2.98	2.96	3.04
Organic	180-200	1.71	1.79	1.76	1.75	1.88
Totals		4.77	4.77	4.81	4.78	4.96

^a HClO_4 - H_3PO_4 (9:1) mixture.

Dissolution of Coal in HClO_4 With Admixtures

In order to obtain even more selectivity, several admixtures were tested with HClO_4 to alter its oxidizing power. One was the addition of H_3PO_4 to promote the dissolution of pyrite and thus extract all pyritic sulfur at a lower temperature without affecting the organic sulfur. In practice, the results were not useful. While the temperature of dissolution was lowered by a few degrees, no further enhancement of differentiation was observed.

The addition of iron salts, however, was more useful. It was anticipated the ferric salts would promote the dissolution of pyrite, as demonstrated by the Meyers process. Catalytic amounts (50-100 mg) of FeCl_3 or $\text{Fe}(\text{ClO}_4)_3$ showed no activity. But when a series of extractions was performed at a lower temperature, at which it is known that HClO_4 by itself does not extract all the pyrite, with increasing amounts of $\text{Fe}(\text{ClO}_4)_3$ added to the mixture and boiled for 1.5 or 2.5 h, the curve depicted in Figure 4 was obtained.

For the extraction of coal with varying amounts of added $\text{Fe}(\text{ClO}_4)_3$ for 1.5 or 2.5 h at 134.5°C, the amount of S removed increased rapidly from 0 to 0.05M $\text{Fe}(\text{ClO}_4)_3$. From 0.05 to 0.7M $\text{Fe}(\text{ClO}_4)_3$, the amount of S removed continued to increase less rapidly, and above 0.7M $\text{Fe}(\text{ClO}_4)_3$ it was fairly constant. These data imply that all the inorganic S could be removed at 134.5°C in the presence of as little as 0.05M $\text{Fe}(\text{ClO}_4)_3$, compared to 143°C required in its absence. They also imply that some organic S form (~0.9%) is labile and can be removed in the presence of <0.7M $\text{Fe}(\text{ClO}_4)_3$ at a temperature of only 134.5°C.

Dissolution of Coals With High Organic Sulfur in HClO_4

For a Spanish lignite (9.63% tot. S, 0.05% sulf. S, 1.06% pyr. S, and 8.52% org. S, as determined by ASTM), a break occurred at ~140°C, corresponding to ~2.5% S; this compares with 1.1% inorganic S by ASTM. Thus, it is very likely that

~1.4% additional (and therefore "organic" sulfur) was dissolved at this temperature. The form of this "organic" sulfur is unknown; it could be noncarbon-bonded sulfur. But the fact is that some form of sulfur that is classified as organic sulfur by ASTM dissolved under these mild conditions. Another break occurred at about 160-167°C corresponding to about 6-7% S, and the remainder of the sulfur dissolved at about 200°C. This would imply that the lignite might contain about 1.1% inorganic S, 1.4% very easily oxidized "organic" S, about 3.5-4.5% organic S that is comparable to that in Illinois No. 6 coal, and about 3-4% organic S which is more difficult to remove. For a specially prepared Bevier seam coal (containing ~3% total S of which ~2.5% is organic S), the results are less easily interpreted. Additional experiments are being carried out to characterize the S forms in more detail.

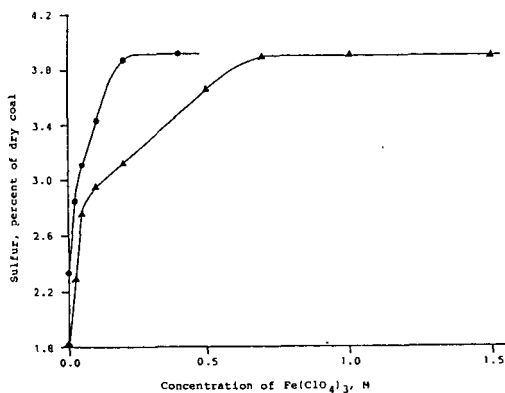


Figure 4. Total sulfur recovered (as percent of dry Illinois No. 6 coal) as a function of $\text{Fe}(\text{ClO}_4)_3$ concentration at 134.5°C

▲ extraction time 1.5 h; ● extraction time 2.5 h

CONCLUSIONS

The delineation of S forms in coal is possible by selective oxidative degradation with boiling HClO_4 . In the plot of total sulfur extracted by boiling HClO_4 of various concentrations, there is a clear delineation between sulfate and pyritic S and between pyritic and organic S. The temperatures at which such differentiations can be made are somewhat lower than previously expected and thus provide better conditions for a more accurate measurement of the various S forms in coal.

The extraction of pyritic S is also directly related to the amount of extracted iron. Organic S is extracted only when oxidative degradation of coal becomes significant, signalling the dissolution of coal, as shown by the deepening color of the extracts and the analyses of the residues.

The presence of $\text{Fe}(\text{ClO}_4)_3$ enhanced the selectivity of HClO_4 in the extraction of sulfur from coal, especially at lower temperatures. Increasing the

$\text{Fe}(\text{ClO}_4)_3$ concentration up to 0.05M allowed the removal of all inorganic sulfur at 134.5°C. Increasing the $\text{Fe}(\text{ClO}_4)_3$ concentration further, up to 0.7M but still at 134.5°C, removed a significant portion of what has to be labile organic S. Further increases in $\text{Fe}(\text{ClO}_4)_3$ concentration did not remove additional organic S. This has to be termed intractable organic S and could be related to the thiophenic-type S.

The HClO_4 dissolution procedure applied to a Spanish lignite with high organic S, showed 4 different forms of S. But specific assignment of functionality to all 4 classes is not as yet possible. Further tests are continuing on this Spanish lignite and on Bevier coal, both containing mostly organic S.

ACKNOWLEDGEMENT

The experimental work was done at Ames Laboratory which is operated for the Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. Most of this work was supported by the Assistant Secretary for Fossil Energy, through the Pittsburgh Energy Technology Center.

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